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CHARACTERIZATION OF LITHIUM FERRO PHOSPHATE CARBON COMPOSITE BY SOLID-STATE REACTION METHODS IN VARIOUS TEMPERATURE CALCINATION

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Abstract

The purification of natural iron stone Tanah Laut has been discovered a high contents of iron, especially magnetite iron (III) oxide (Fe_3O_4). This material is proposed for raw material of Lithium iron phosphate $LiFePO_4$ by a simple solid-state reaction method. The solid-state reaction method was conducted by milling used raw materials of Fe_3O_4, Li_2CO_3 (merck), and $(NH_4)_2HPO_4$ (merck) with a powder-ball ratio 1:6 for 7 hours in room temperature. The precursor of lithium iron phosphate has been calcinations with various temperature at 500ºC, 600ºC, and 700ºC for 10 hour. The lithium iron phosphate characterized by X-ray powder diffraction (XRD) and Particle Size Analyzer (PSA) to determine the phase and the distribution particle size of lithium iron phosphate. Analyze result on XRD pattern obtain more stable ortorhombic phase of $LiFePO_4$ at 700°C. The impurities phase of monoclinic $LiFeP_2O_7$, $Li_2FeP_2O_7$ and hematite phase gradually decreased and vanish in higher temperature. The distribution particle size obtained inhomogeneous particle sizes in range 200-300 nm.

Key words: iron stone, magunetite, solid-state reaction methods, lithium iron phosphate

INTRODUCTION

There are many types of energy storage technologies avaiable based on mechanical, electrical, chemical and electrochemical modes. Among those, electrochemical energy storage based on batteries is very promising. Replacing the internal combustion engine (ICE) vehicles with electric vehicles (EVs) and hybrid electric vehicles (HEVs) is a possible way to mitigate CO_2 emission in the future [1]. Therefore, The development of more efficient, convenient, pollution-free, high energy density, high power density, and high safety of rechargeable batteries is particulary interest to fullfil the human needs.

The development of Lithium-ion batteries have been considered to analyze, model and control battery behaviors [2-5]. There are a lots of secondary batteries but Lithium-ion batteries is one of promising energy storage devices for portable electronics, electrified vehicles and renewable energy storage. The secondary batteries have components such as anode, cathode, electrolyte, and separator, this study focused on researching the chatode material.

The $LiFePO_4$ has attracted because of high theoretical charging capacity, good cycle stability, excellent thermal stability and environmental friendly. However, the charge/discharge capacity of LFP is generally much lower than the theoretical value, especially at high current rates, and it has two major disadvantages of poor electronic conductivity and slow diffusion of lithium ions [6, 7] but it can be done by reducing particle size and added carbon coating [8-10].

LFP/C was synthesized by a lot of methods such as co-precipitation method [11], Solid-state method [10], sol-gel [12], microwave heating [13], and Hydrothermal method [14]. In this study, reseacher used solid-state reaction methods using high energy ball milling. The solid-state reaction methods has some distinct advantages over the other methods, such a simple synthesis process, well-known and appropriate for mass production. All of these methods generally have *proanalis* as raw materials to formed LFP such as Li_2CO_3, LiH_2PO_4, $LiOH.H_2O$, $CH_3COOLi.2H_2O$, etc as Li^+ sources, $(NH_4)_2HPO_4$, $FePO4.2H_2O$, $NH_4H_2PO_4$ as PO_4 sources, and $FeC_2O_4.2H_2O$, $FeSO_4$, Fe $(CH_3COO)_2$, Fe_2O_3, $Fe(NO_3)_3$ as Fe-sources even some of them are expensive and toxic.

Based on investigated of iron rock in Tanah Laut Kalimantan with XRF that indicated of high content of Fe and the result of XRD was found that the natural iron stone contained magnetite Fe_3O_4. Mineral Fe_3O_4 will be a very bright prospect as a major source of Fe-source material for chatode. Hence, researcher tried to use natural iron stone Fe_3O_4 as Fe sources to form LiFePO4/C to avoid high-cost in Fe source.

RESEARCH METHOD

This research was started from the preparation of iron stone collected from Tanah Laut, Kalimantan. The Iron stone was crush and separated by magnet to obtain the magnetic particles. After magnetic separation, it was washed with alcohol by an ultrasonic cleaner for 5 times until impurities removed and reach a black bulk precursor. The elements of Fe in the bulk of iron stone were qualitatively confirmed by X-ray Fluorescence (XRF) analysis and for phase Fe_3O_4 were confirmed by X-ray powders diffraction (XRD).

The $LiFePO_4$/C composites was prepared by the solid-state methods using high energy ball milling with the starting materials are Li_2CO_3, $(NH_4)2HPO4$, Fe_3O_4, and citric acid as carbon sources. More details are describes as follows. First, crash iron rock until become bulk then separating using magnet. Bulk precursors of iron stone were dissolved in aqueous solution using ultrasonic cleaner to remove impurities. Phase form of bulk examined by X-ray powder diffraction (XRD) to confirm magnetite phase.

Then, Li_2CO_3, $(NH_4)_2HPO4$, Fe_3O_4, citrid acid and alcohol as reducing agents were mixed with zirconia milling beads in a stoichiometric molar ratio 3:6:2. The weight of carbon source was 5wt% of the total raw materials, adding as the conducting enhancer and to avoid oxidation. Material milled for 4 hour with ball-to-powder ratio in ethanol was fixed at 5:1, and the rotating speed was 300 rpm.

The calcinations temperature was investigate by DSC-TGA. Heat treatment is given on the sample to determine the phase transformation. The Sample was given calcinations temperature at 500°C, 600°C, and 700° for 10 hours. In order to avoid oxidation, the preparation of LFP/C composites was conducted under N_2 atmosphere. X-ray powders diffraction (XRD) Rigaku was adopted to identify crystalline phases and composition on the samples. The distribution and homogenitas size was identified by Particle Size Analyzer (PSA).

RESULT AND DISCUSSION

X-ray fluorescence (XRF) analysis of it reveals that the bulk precusor of iron stone contains Fe 98.02wt%, Si 1 wt%, Ca 0.1 wt%, V 0.03 wt%, Cr 0.097 wt%, Mn 0.13 wt%, Cu

0.04 wt%, and Br 0.55 wt%. The XRD pattern of the iron stone after passed the preparation steps is shown in Fig. 1. It indicated cubic Fe_3O_4 (PDF-4, 04-015-3102) with space group 227:Fd-3m. The refinement of the zirconia powder XRD patterns structural parameter was carried out by PDXL software.

Thermal properties of LFP_4/C composites were analyzed by DSC-TGA in room temperature until 1300°C. Heat flow diagram in Fig. 2. shows that there is a thermal phenomenon at range temperature 400°C until 700°C. In this range temperatures indicate there are phases transform occur along the increasing of thermal treatment.

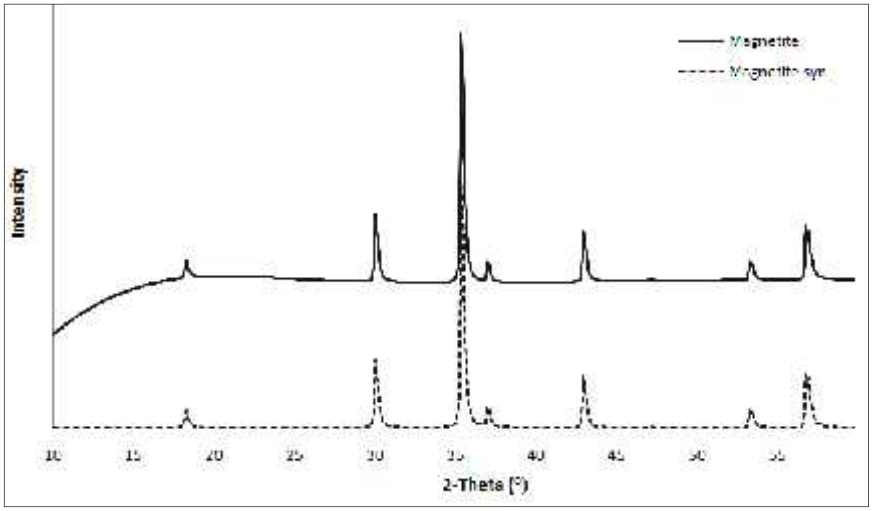


Fig. 1. The XRD pattern of Fe_3O_4 bulk after preparation

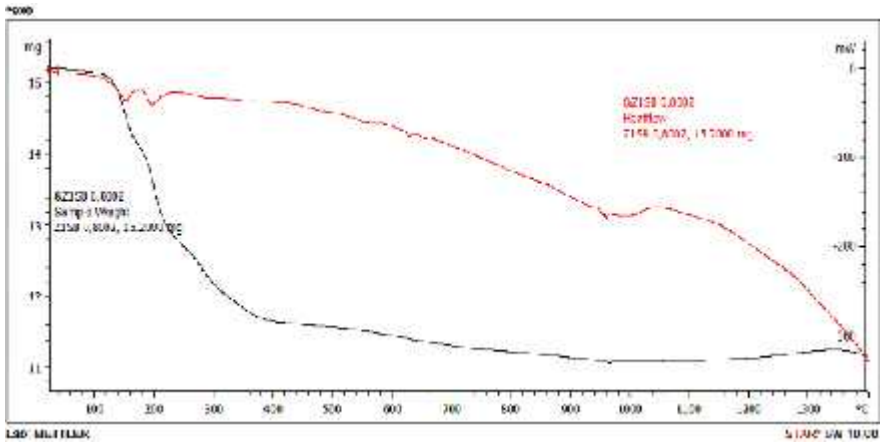


Fig. 2. The DSC-TGA curve of precusor LFP/C composites by ball-milling methods

In this paper carbon source in the LFP/C composites synthesis process had functions as reducing agent for Fe^{3+} into Fe^{2+}, it's could reduce the number of raw materials, restrain in the growth of the $LiFePO_4$ particles and carbon material to enchance the electronic conductivity of the composites. In order to study the variated calcination temperature affected on crystalline phase of the synthesized $LiFePO_4$/C composites, the X-ray diffraction (XRD) pattern of the LFP/C with citrid acid as carbon source shown in Fig. 3.

The diffraction peak in the XRD pattern reveals impurities in sample that calcined at 400°C and 500°C. The hematite phase appear along metastable phase of monoclinic $LiFeP_2O_7$ at 400°C, when the temperature reach 500°C the monoclinic $LiFeP_2O_7$ phase vanish but hematite still remain, however hematite phase completely removed at 600°C. The single peak of $LiFePO_4$ obtained at temperature 700°C (ICDDno. 04-015-6173). The residual carbon in the LFP/C composite was amorphous, it has no influence on the crystallinity of the composite material. The results of refinement analysis of LFP/C powder in each sample are shown in Table 1.

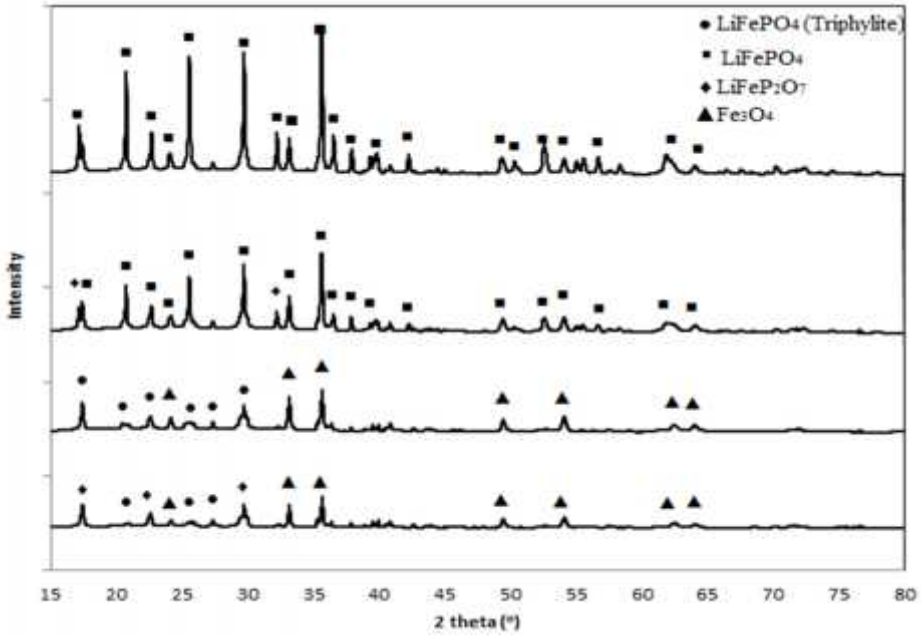
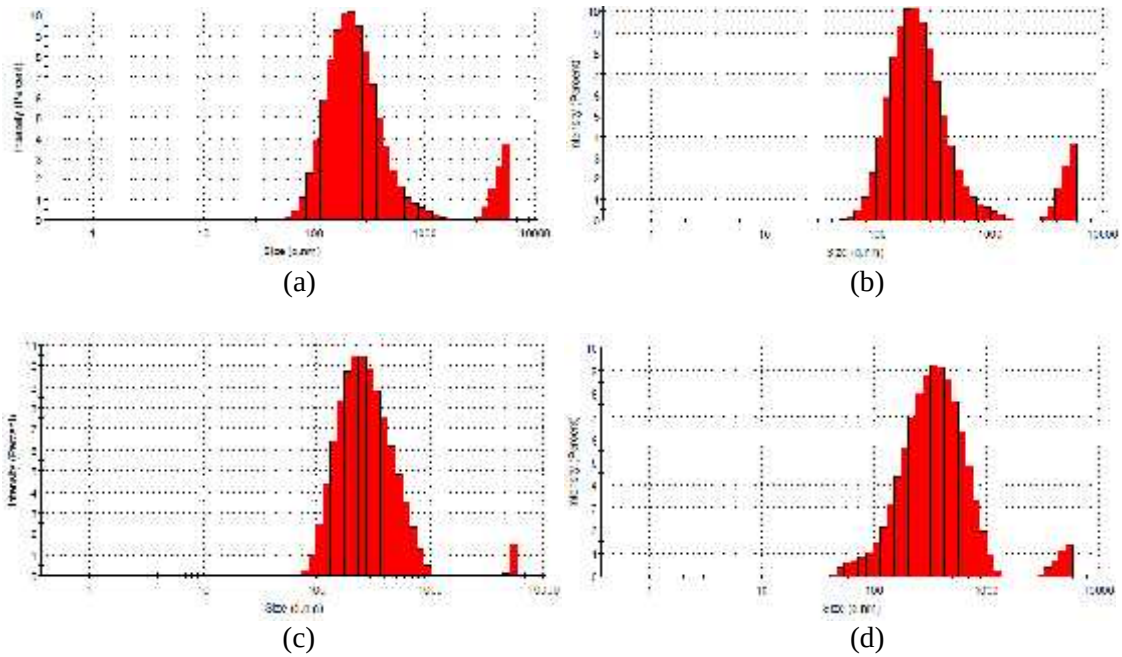


Fig. 3. The XRD pattern of LFP/C composites by solid-state reaction methods at 400°C, 500°C, 600°C, and 700°C

Table 1. The results of refinement analysis of LFP/C powder.

Sample $LiFePO_4$/C at	Phase (Space Group)	No. ICDD	% Weight Phase Composition
400°C	$LiFePO_4$ (62/Pnma)	00-040-1499	31
	$LiFeP_2O_7$ (P1211)	04-011-6388	48
	Fe_3O_4 (R-3c)	00-033-0664	21
500°C	$LiFePO_4$ (62/Pnma)	04-015-7065	62
	Fe_3O_4 (R-3c)	01-080-5409	38
600°C	$LiFePO_4$ (62/Pnma)	01-080-6319	69
	$Li_2FeP_2O_7$ (P121/c1)	04-017-3008	31
700°C	$LiFePO_4$ (62/Pnma)	04-015-6173	100

The homogeneous particle size details after heat treatment was detected by Particle Size Analyzer (PSA). From the result, it is obviously that the particle size become larger with the increase of calcined temperature. The sample synthesized with solid-state reaction methods presented some big particles and some small ones with inhomogeneous particle sizes in range 200-300 nm. The detail are shown in Fig. 4. The smaller particles could shorten the transport path of Li^+ ions, increase the specific area of LFP/C composites and increasing the contact area between Li^+ ions and electrolyte solution.



(a) (b)

(c) (d)

Fig. 3. Particle size distribution of the LFP/C composite after calcined at (a) 400°C (b) 500°C, (c) 600°C, and (d) 700°C.

CONCLUSION AND SUGGESTION

The varied calcination temperature applied on the sample determine the phase and the composition amount. Analyze result on XRD pattern obtain more stable ortorhombic phase of $LiFePO_4$ at 700°C. The impurities phase of monoclinic $LiFeP_2O_7$, $Li_2FeP_2O_7$ and hematite phase gradually decreased and vanish in higher temperature. The distribution particle size obtained inhomogeneous particle sizes in range 200-300 nm. The increasing calcination temperature influence the particle size of particle. It is disadvatanges for Li^+ ions difusion, larger particles couldn't shorten the transport path Li^+ ions. The emergence of the impurities phase can be overcome by providing a change at holding time calcination. Meanwhile. A more homogeneous particle distribution can be obtained by increasing the holding of milling time and using small rate at temperature calcinacion.

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